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Thermal stability of tungsten sub-nitride thin film prepared by reactive magnetron sputtering

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ABSTRACT

Tungsten sub-nitride thin films deposited on silicon samples by reactive magnetron sputtering were used as a model system to study the phase stability and microstructural evolution during thermal treatments. XRD, SEM&FIB, XPS, RBS and TDS were applied to investigate the stability of tungsten nitride films after heating up to 1473 K in vacuum. At the given experimental parameters a 920 nm thick crystalline film with a tungsten and nitrogen stoichiometry of 2:1 were achieved. The results showed that no phase and microstructure change occurred due to W_2N film annealing in vacuum up to 973 K. Heating up to 1073 K led to a partial decomposition of the W_2N phase and the formation of a W enrichment layer at the surface. Increasing the annealing time at the same temperature, the further decomposition of the W_2N phase was negligible. The complete decomposition of W_2N film happened as the temperature reached up to 1473 K.

1. Introduction

Carbon is increasingly being replaced by metallic plasma-facing surfaces in fusion machines. Due to its favorable physical properties, such as low sputtering yield, low hydrogen solubility and high melting temperature, tungsten is the most promising high-Z plasma-facing material (PFM) for ITER and next step fusion reactors such as DEMO [1,2]. With the transition from carbon to tungsten wall the lack of radiation from C in the edge plasma leads to an increase in the power flux to the divertor [3]. To mitigate the heat loads to the divertor targets by radiative power dissipation, it will therefore be necessary to replace intrinsic carbon by the injection of seeding impurity gases [3–9]. In recent years, impurity gas seeding as radiator to reduce thermal load on the PFM has been received high attention and extensive research in fusion field [4]. Nitrogen has favorable radiation properties, and could reduce the power flux to the divertor targets [7]. Studies in ASDEX Upgrade and JET found that nitrogen seeding in fusion plasma could obviously improve the performance of plasma and reduce tungsten sputtering [3,6,8]. Nevertheless, general issues of nitrogen seeding in fusion plasma are the nitrogen ion implantation into plasma-facing materials, re-deposition with tungsten and ammonia formation [9]. Tungsten nitride could then be decomposed and sudden release of large amounts of nitrogen from the walls in subsequent discharges, which could lead to a sudden termination of plasma operation. So the temperature stability of tungsten nitrides present at tungsten surfaces is an important aspect for the application of nitrogen in fusion experiments. Both amorphous and crystalline W-N films synthesized by different methods have been extensively studied. Structural and electrical characteristics of W-N thin films prepared by reactive radio frequency (RF) sputtering at room temperature with different bias on substrate, sputtering power and N_2 partial flow rate were exampled in detail by Jiang et al. [10]. Other researchers have studied resistivity changes and phase evolution of tungsten nitride in Ne-N_2 and Ar-N_2 discharges [11], chemical-state configuration of elements, surface morphology, and residual stress under different preparation conditions [12–15]. However, under the condition of high vacuum the published information about the changes of morphology, crystal structure, and

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composition of the tungsten nitride with the temperature increases is limited, while these are essential for application of nitrogen in cooling the edge plasma and the designing of PFM.

In this paper, tungsten nitride film with a thickness of 920 nm was prepared using magnetron sputtering, and then the microstructural and compositional changes of tungsten nitride films as the function of annealing temperature and duration were investigated.

2. Experimental details

The tungsten nitride films were deposited on single-crystalline (100) silicon samples by reactive RF-magnetron sputtering of W target (99.99% purity with 75 mm in diameter and 8 mm thickness) in the Ar-N_2 mixed atmosphere. The base pressure of chamber was pumped down to below 1×10^{-3} Pa and during deposition the pressure of the system was kept at 0.5 Pa. The distance from substrate to target was 80 mm, and in the whole deposition process the substrate holder was not cooled or heated additionally. Prior to film deposition the substrate was cleaned using argon plasma by applying a 500 V negative bias voltage. Then the tungsten target was pre-sputtered for 10 min at 0.5 Pa argon atmosphere by applying 350 W RF power. Finally, tungsten nitride films were deposited in argon and nitrogen mixed atmosphere with 40 and 30 sccm (standard cubic centimeter per minute) flow rates respectively.

To ensure a homogeneous thickness for all the samples, all tungsten nitride film samples used in this work were deposited in one batch, and the substrate holder was rotating through the whole deposition process. The variation of the film thickness over the fixed deposition area was within 5% [16]. The film thickness determined by SEM cross-sectional images is 920 nm with 10 nm variation due to surface roughness. After deposition the sample was annealed at different temperatures and annealing durations.

Sample annealing treatments up to 1273 K were carried out in a quartz tube vacuum oven. Prior to annealing treatment, the system was pumped down to a base pressure of less than 1×10^{-5} Pa. Each sample was heated to an annealing temperature with a heating rate of 10 K/min and kept for 30 min at the maximum temperature. The temperature of the sample was calibrated in the independent experiment by a thermocouple fixed to a sample with identical size. The maximum achievable temperature in this quartz tube oven was 1273 K.

Further annealing up to a higher temperature was performed in the second high vacuum oven, and this device was used for thermal desorption spectroscopy (TDS) investigation, in which the sample temperature could be increased up to 1473 K using tungsten filament heating. Prior to annealing treatment, the system was pumped down to a base pressure of less than 1×10^{-6} Pa. After prior outgassing of the sample holder, the sample was moved to the measurement position by a remote control arm in the chamber. The decomposition of tungsten nitride films during annealing was monitored by temperature programmed desorption device. The 920 nm thick crystalline film samples were heated up to a temperature of 1473 K with a heating rate of 30 K/min. The sample temperature was in-situ measured. The desorbed gases were recorded with a quadrupole mass spectrometer (QMS). The secondary electron multiplier of the QMS was operated in single ion counting mode. Selected mass channels between 7 and 44 amu were recorded by the QMS as a function of time.

Crystallographic structure and composition of the films before and after annealing were investigated by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Rutherford backscattering spectroscopy (RBS). XRD measurements were performed on a Rigaku RINT2400 X-ray diffractometer using Cu Kα radiation with $\lambda = 1.54056$ Å. Scanned over the range 10–90° 2θ at steps of 0.03° at a 0.1° receiving slit. Film composition was determined by X-ray photoelectron spectroscopy (XPS, PHI-5720) using a hemispherical energy analyzer equipped with monochromatic Al Ka radiation at a pass energy of 29.4 eV. The XPS spectra were referenced with respect to C 1s line at 284.8 eV. Prior to measurement a 3 keV Ar^+ ion beam was used to clean the surface contamination due to air exposure. RBS analysis was also performed to measure the composition changes of the tungsten nitride film due to annealing. A silicon surface barrier detector was placed at the backscattering angle of 160°. Samples were fixed on the target plate using a conductive adhesive tape, and then a wire that coming from the target plate was led to the beam integrator to measure the beam. A beam of 3 MeV $^4He^+$ was used at a scattering angle of 160°, and a charge of 15 μC was usually accumulated for one RBS spectrum. The obtained spectra were simulated using the program SIMNRA 6.05 code [17]. Surface and cross-section images of the films were investigated by scanning electron microscopy combined with focused ion beam (SEM&FIB). The used microscope (Helios Nano-Lab 600, FEI) allowed the cross-sectioning in situ by the implemented 30 keV singly charged Ga^+ focused ion beam. The secondary electrons produced by a 5 keV electron beam were detected by the in lens detector system. The cross sections were imaged with the e-beam tilted by 38° to their surface plane, so that the vertical scale in the images was not equal to the horizontal scale. The thickness values given in later sections were converted (calculated as: $d_h = d_v/\sin 38°$) into the horizontal scale. Before the cross-sectioning by FIB, a Pt composite strip was deposited as a mask for protection of area of interest during FIB milling. The in-situ scanning electron microscopy imaging was performed with an accelerating voltage of 5 kV under a beam current of 86 pA. The cross section was examined with the electron beam incident tilt angle of 52°.

3. Results and discussions

3.1. Crystal structure of deposited film

Tungsten sub-nitride films used in this study were produced by magnetron sputtering of a tungsten target in the nitrogen and argon atmosphere. The XRD patterns of tungsten sub-nitride films compared with a pure tungsten film are shown in Fig. 1. The

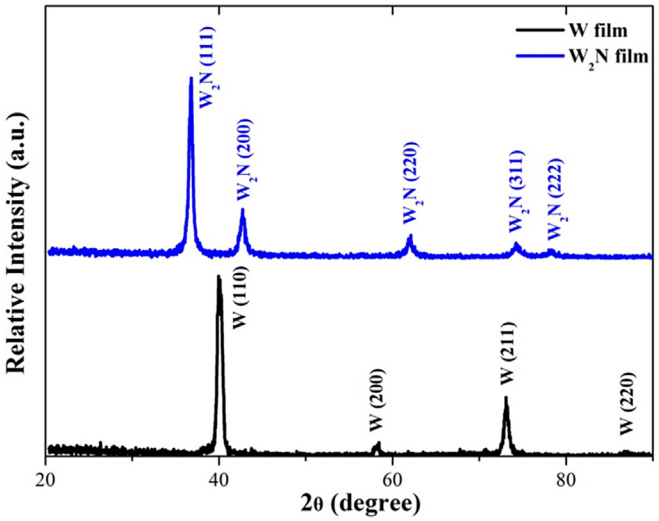

Fig. 1. X-ray diffraction patterns of as-deposited W and W_2N films.